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(54) Catalyst component for polymerization of olefins.

(57) A catalyst component for the polymerization of olefins which is prepared by contacting (1) a contact reaction product of (a) a metal oxide, (b) a dihydrocarbyl magnesium, and (c) a halogen-containing alcohol held with (d) an electron-donating compound, and (e) a titanium compound.

**EP 0 171 200 A2**

# CATALYST COMPONENT FOR POLYMERIZATION OF OLEFINS

2           This invention relates to a catalyst component for the  
3 polymerization of olefins and, to the catalyst system comprising the  
4 catalyst component, and to the process of polymerizing olefins,  
5 especially olefins having 3 or more carbon atoms, in the presence of  
6 the catalyst system.

## 7 BACKGROUND OF THE INVENTION:

8           Concerning Ziegler-Natta type catalysts which are effective  
9 in polymerizing olefins, catalyst components having transition metals  
10 deposited on a variety of carriers have been developed for the purpose  
11 of improving catalyst activity per unit amount of catalyst or decreas-  
12 ing residues originating in catalyst and persisting in produced  
13 polymer.

14           A plurality of catalyst components using silica, alumina, and  
15 other similar metal oxides as carriers for deposition of transition  
16 metals have been proposed. Most of them are intended for polymeriza-  
17 tion of ethylene. A very few of them are intended for polymeriza-  
18 tion of alpha-olefins such as propylene.

19           As concerns catalyst compositions for the polymerization of  
20 propylene, a catalyst component comprising a reaction product of a  
21 metal oxide and a magnesium dialkoxide brought in contact with an  
22 electron-donating compound and a tetravalent titanium halide (specifi-  
23 cation of Japanese Patent Application Laid-open SHO 58[1973]-162,607)  
24 and a catalyst component comprising a reaction product of an inorganic  
25 oxide and a magnesium hydrocarbyl halide compound brought in contact  
26 with a Lewis base compound and titanium tetrachloride (specification  
27 of Japanese Patent Application Laid-open SHO 55[1980]-94,909) are  
28 known to the art. These catalyst components, however, can hardly be  
29 called satisfactory in terms of activity and stereoregularity.

30           Further, a catalyst component obtained by causing a  
31 hydrocarbyloxysilane to react with a reaction product of a porous  
32 carrier such as silica and an alkyl magnesium compound and subse-  
33 quently causing a titanium halide compound to react upon the resultant  
34 reaction product (specification of Japanese Patent Application Laid-  
35 open SHO 57[1982]-153,006) and a catalyst component obtained by  
36 causing an organic metal compound to react with a porous carrier,

1 causing a hydrocarbyl alcohol to react with the resultant reaction  
2 product, and then causing a titanium halide compound to react with the  
3 reaction product (specification of Japanese Patent Application  
4 Laid-open SHO 57[1982]-200,408) have been proposed. These catalyst  
5 components are intended for homopolymerization of ethylene or for  
6 copolymerization of ethylene with other olefins. They are not  
7 suitable for polymerization of alpha-olefins such as propylene.

8 DISCLOSURE OF THE INVENTION

9

10 It is an object of this invention to provide a catalyst  
11 component which uses a metal oxide as a carrier and which is used for  
12 homopolymerization of an olefin exhibiting high activity and high  
13 stereoregularity, particularly an alpha-olefin such as propylene, and  
14 for copolymerization of the aforementioned olefin with other olefins.  
15 More particularly, in accordance with an object of this invention  
16 there is provided a catalyst component which is prepared by contact-  
17 ing a contact reaction product of a metal oxide, a dihydrocarbyl  
18 magnesium, and a halogen-containing alcohol held in contact with an  
19 electron-donating compound and a titanium compound.

20

23 To be specific, this invention essentially concerns a  
24 catalyst component for the polymerization of olefins which is prepared  
25 by contacting a contact reaction product of (1) (a) a metal oxide, (b)  
26 a dihydrocarbyl magnesium, and (c) a halogen-containing alcohol  
27 with (2) (d) an electron-donating compound and (e) a titanium  
28 compound.

29 Raw materials for preparation of catalyst component

30 (A) Metal Oxide

31 The term "metal oxide" is used in this invention to refer  
32 to oxides of elements in Groups II, III and IV in the  
33 Periodic Table of Elements. Examples of the oxide  
34 are  $B_2O_3$ ,  $MgO$ ,  $Al_2O_3$ ,  $SiO_2$ ,  $CaO$ ,  $TiO_2$ ,  $ZnO$ ,  $ZrO_2$ ,  $SnO_2$ ,  $BaO$ , and  
35  $ThO_2$ . Among other oxides enumerated above,  $B_2O_3$ ,  $MgO$ ,  $Al_2O_3$ ,  $SiO_2$ ,  
36  $TiO_2$ , and  $ZrO_2$  are more desirable selections, and  $SiO_2$  is the most  
37 desirable selection. Further, composite oxides including these metal  
38 oxides are also usable. Examples of these composite oxides are

1  $\text{SiO}_2\text{-MgO}$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-TiO}_2$ ,  $\text{SiO}_2\text{-V}_2\text{O}_5$ ,  $\text{SiO}_2\text{-Cr}_2\text{O}_3$ , and  
2  $\text{SiO}_2\text{-TiO}_2\text{-MgO}$ .

3 The aforementioned metal oxides or composite oxides described  
4 above are desirably anhydrous. The invention,  
5 tolerates inclusion of a hydroxide in a very small amount normally  
6 entrained in the metal oxide of the class under discussion. It also  
7 tolerates inclusion therein of impurities to an extent incapable of  
8 appreciably impairing the nature of metal oxide. Examples of the  
9 impurities so tolerated are oxides, carbonates, sulfates, and nitrates  
10 such as sodium oxide, potassium oxide, lithium oxide, sodium carbon-  
11 ate, potassium carbonate, calcium carbonate, magnesium carbonate,  
12 sodium sulfate, aluminum sulfate, barium sulfate, potassium nitrate,  
13 magnesium nitrate, and aluminum nitrate.

14 Generally, the metal oxide of the foregoing description is  
15 used in the form of powder. The size and shape of the individual  
16 particles of this powder are desired to be suitably adjusted because  
17 they often have bearing on the shape of the olefin polymer to be  
18 produced. Prior to use, this metal oxide is fired at  
19 appropriately high temperature to expel poisoning  
20 substances and then held so as not to be exposed to the  
21 atmosphere.

## 22 (B) Dihydrocarbyl Magnesium

23 The dihydrocarbyl magnesium to be used in the present inven-  
24 tion (hereinafter referred to as "organic Mg") may be represented by the  
25 general formula,  $\text{RMgR}'$ . In this formula, R and R', which can be the  
same or different, preferably denote an alkyl, cycloalkyl,  
aryl, or aralkyl group of 1 to 20 carbon atoms.

28 Examples of the organic Mg are dimethyl magnesium (herein-  
29 after "magnesium" will be abbreviated "Mg"), diethyl Mg, ethylmethyl  
30 Mg, dipropyl Mg, diisopropyl Mg, ethylpropyl Mg, dibutyl Mg, diiso-  
31 butyl Mg, di-sec-butyl Mg, di-tert-butyl Mg, butylethyl Mg, butyl-  
32 propyl Mg, sec-butylethyl Mg, tert-butylisopropyl Mg, sec-butyl-tert-  
33 butyl Mg, dipentyl Mg, diisopentyl Mg, ethylpentyl Mg, isopropylpentyl  
34 Mg, sec-butylpentyl Mg, dihexyl Mg, ethylhexyl Mg, butylhexyl Mg,  
35 tert-butylhexyl Mg, (2-ethylbutyl)ethyl Mg, (2,2-diethylbutyl)ethyl  
36 Mg, diheptyl Mg, dioctyl Mg, di-2-ethylhexyl Mg, didecyl Mg, dicyclo-  
37 hexyl Mg, cyclohexylethyl Mg, butylcyclohexyl Mg, di(methylcyclohexyl)  
38 Mg, diphenyl Mg, ethylphenyl Mg, butylphenyl Mg, sec-butylphenyl Mg,

1 ditolyl Mg, ethyltolyl Mg, dixyllyl Mg, dibenzyl Mg, benzyl-tert-butyl  
2 Mg, diphenethyl Mg, and ethylphenethyl Mg.

Th organic Mg may be a mixture of dihydrocarbyl magnesium compounds or a complex, or a mixture with an organic compound of other metal, such as a compound of the general formula  $MR_n$  (wherein M denotes boron,)

6 beryllium, aluminum, or zinc, R denotes an alkyl, cycloalkyl, aryl, or  
7 aralkyl group of 1 to 20 carbon atoms, and n denotes the valency of  
8 the metal M). Examples of the organic compound of other  
9 metals are triethyl aluminum, tributyl aluminum, triisobutyl aluminum  
10 triphenyl aluminum, triethyl boron, tributyl boron, diethyl beryllium  
11 diisobutyl beryllium, diethyl zinc, and dibutyl zinc.

12 In the aforementioned mixture or complex compound, the ratio  
13 of the organic Mg to the organic compound of other metal generally is  
14 such that the amount of the other metal is not more than 5 gram atoms  
15 preferably not more than 2 gram atoms, per gram atom of magnesium.

#### 16 (C) Halogen-containing Alcohol

17 The term "halogen-containing alcohol" as used in this invention means a monohydric or polyhydric alcohol, thus possessing one or more hydroxyl groups in the molecule thereof having one or more hydrogen atoms thereof other than the aforementioned hydroxyl group substituted with a halogen atom. Examples of the halogen atom are chlorine, bromine, iodine, and fluorine atom. Among the

23 halogen atoms cited above, the chlorine atom is particularly desirable

24 Examples of the halogen-containing alcohol are 2-chloro-  
25 ethanol, 1-chloro-2-propanol, 3-chloro-1-propanol, 1-chloro-2-methyl-  
26 2-propanol, 4-chloro-1-butanol, 5-chloro-1-pentanol, 6-chloro-1-  
27 hexanol, 3-chloro-1,2-propane diol, 2-chlorocyclohexanol, 4-chloro-  
28 benzhydrol, (m,o,p)-chlorobenzyl alcohol, 4-chlorocatechol, 4-chloro-  
29 (m,o)-cresol, 6-chloro-(m,o)-cresol, 4-chloro-3,5-dimethylphenol,  
30 chlorohydroquinone, 2-benzyl-4-chlorophenol, 4-chloro-1-naphthol,  
31 (m,o,p)-chlorophenol, p-chloro-alpha-methylbenzyl alcohol, 2-chloro-  
32 4-phenylphenol, 6-chlorothimol, 4-chlororesorcin, 2-bromoethanol,  
33 3-bromo-1-propanol, 1-bromo-2-propanol, 1-bromo-2-butanol, 2-bromo-  
34 p-cresol, 1-bromo-2-naphthol, 6-bromo-2-naphthol, (m,o,p)-bromo-  
35 phenol, 4-bromoresorcin, (m,o,p)-fluorophenol, p-iodophenol:  
36 2,2-dichloroethanol, 2,3-dichloro-1-propanol, 1,3-dichloro-2-propanol  
37 3-chloro-1-(alpha-chloromethyl)-1-propanol, 2,3-dibromo-1-propanol,  
38 1,3-dibromomono-2-propanol, 2,4-dibromophenol, 2,4-dibromo-1-naphtho

2,2,2-trichloroethanol, 1,1,1-trichloro-2-propanol, B,B,B-trichloro-tert-butanol, 2,3,4-trichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,4,6-tribromophenol, 2,3,5-tribromo-2-hydroxy toluene, 2,3,5-tribromo-4-hydroxy toluene, 2,2,2-trifluoroethanol, alpha,alpha,alpha-trifluoro-m-cresol, 2,4,6-triiodophenol: 2,3,4,6-tetrachlorophenol, tetrachlorohydroquinone, tetrachloro-bis-phenol A, tetrabromo-bis-phenol A, 2,2,3,3-tetrafluoro-1-propanol, 2,3,5,6-tetrafluorophenol, and tetrafluororesorcin.

(D) Electron-donating Compound

Examples of the electron-donating compound are carboxylic acids, carboxylic anhydrides, carboxylic esters, carboxylic halides, alcohols, ethers, ketones, amines, amides, nitriles, aldehydes, alcoholates, phosphorus, bismuth, and antimony compounds linked with organic groups through the medium of carbon or oxygen atom, phosphamides, thioethers, thioesters, and carbonic esters. Among other electron-donating compounds cited above, carboxylic acids, carboxylic anhydrides, carboxylic esters, carboxylic halides, alcohols and ethers are particularly desirable.

Concrete examples of the carboxylic acids are aliphatic monocarboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, pivalic acid, acrylic acid, methacrylic acid, and crotonic acid, aliphatic dicarboxylic acids such as malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, maleic acid, and fumaric acid, aliphatic oxycarboxylic acids such as tartaric acid, alicyclic carboxylic acids such as cyclohexane monocarboxylic acids, cyclohexene monocarboxylic acids, cis-1,2-cyclohexane dicarboxylic acids, and cis-4-methylcyclohexane-1,2-dicarboxylic acids, aromatic monocarboxylic acids such as benzoic acid, toluic acid, anisic acid, p-tert-butyl-benzoic acid, naphtholic acid, and cinnamic acid, and aromatic poly carboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, naphthalic acid, trimellitic acid, hemimellitic acid, trimestic acid, pyromellitic acid, and mellitic acid.

Concrete examples of carboxylic anhydrides are the anhydrides of the carboxylic acids enumerated above.

Carboxylic esters are monoesters and polyesters of the carboxylic acids enumerated above. Concrete examples of such monoesters and polyesters are butyl formate, ethyl acetate, butyl acetate, iso-

1 butyl isobutyrate, propyl pivalate, isobutyl pivalate, ethyl acrylate,  
 2 methyl methacrylate, ethyl methacrylate, isobutyl methacrylate,  
 3 diethyl malonate, diisobutyl malonate, diethyl succinate, dibutyl  
 4 succinate, diisobutyl succinate, diethyl glutarate, dibutyl glutarate,  
 5 diisobutyl glutarate, diisobutyl adipate, dibutyl sebacate, diisobutyl  
 6 sebacate, diethyl maleate, dibutyl maleate, diisobutyl maleate,  
 7 monomethyl fumarate, diethyl fumarate, diisobutyl fumarate, diethyl  
 8 tartrate, dibutyl tartrate, diisobutyl tartrate, ethyl cyclohexane-  
 9 carboxylates, methyl benzoate, ethyl benzoate, methyl p-toluate, ethyl  
 10 p-tert butylbenzoate, ethyl p-anisate, ethyl alpha-naphthoate, iso-  
 11 butyl alpha-naphthoate, ethyl cinnamate, monomethyl phthalate,  
 12 monobutyl phthalate, dibutyl phthalate, diisobutyl phthalate, dihexyl  
 13 phthalate, dioctyl phthalate, di-2-ethylhexyl phthalate, diallyl  
 14 phthalate, diphenyl phthalate, diethyl isophthalate, diisobutyl  
 15 isophthalate, diethyl terephthalate, dibutyl terephthalate, diethyl  
 16 naphthalate, dibutyl naphthalate, triethyl trimellate, tributyl  
 17 trimellate, tetramethyl pyromellate, tetraethyl pyromellate, and  
 18 tetrabutyl pyromellate.

19 Carboxylic halides are halides of the carboxylic acids  
 20 enumerated above. Concrete examples of such halides are acetic acid  
 21 chloride, acetic acid bromide, acetic acid iodide, propionic acid  
 22 chloride, butyric acid chloride, butyric acid bromide, butyric acid  
 23 iodide, pivalic acid chloride, pivalic acid bromide, acrylic acid  
 24 chloride, acrylic acid bromide, acrylic acid iodide, methacrylic acid  
 25 chloride, methacrylic acid bromide, methacrylic acid iodide, crotonic  
 26 acid chloride, malonic acid chloride, malonic acid bromide, succinic  
 27 acid chloride, succinic acid bromide, glutaric acid chloride, glutaric  
 28 acid bromide, adipic acid chloride, adipic acid bromide, sebacic acid  
 29 chloride, sebacic acid bromide, maleic acid chloride, maleic acid  
 30 bromide, fumaric acid chloride, fumaric acid bromide, tartaric acid  
 31 chloride, tartaric acid bromide, cyclohexane-carboxylic acid chloride  
 32 cyclohexane-carboxylic acid bromides, 1-cyclohexene-carboxylic acid  
 33 chloride, cis-4-methylcyclohexene-carboxylic acid chloride, cis-4-  
 34 methylcyclohexene-carboxylic acid bromide, benzoyl chloride, benzoyl  
 35 bromide, p-toluic acid chloride, p-toluic acid bromide, p-anisic acid  
 36 chloride, p-anisic acid bromide, alpha-naphthoic acid chloride,  
 37 cinnamic acid chloride, cinnamic acid bromide, phthalic acid  
 38 dichloride, phthalic acid dibromide, isophthalic acid dichloride,



1 isophthalic acid dibromide, terephthalic acid dichloride, and  
2 naphthalic acid dichloride. Further monoalkylhalides of dicarboxylic  
3 acids such as adipic acid monomethyl chloride, maleic acid monoethyl  
4 chloride and maleic acid monomethyl chloride and phthalic acid butyl  
5 chloride are also usable.

6 Alcohols are represented by the general formula ROH. In the  
7 formula, R denotes an alkyl, alkenyl, cycloalkyl, aryl, or aralkyl  
8 group of 1 to 12 carbon atoms. Concrete examples of such alcohols are  
9 methanol, ethanol, propanol, isopropanol, butanol, isobutanol,  
10 pentanol, hexanol, octanol, 2-ethylhexanol, cyclohexanol, benzyl  
11 alcohol, allyl alcohol, phenol, cresol, xlenol, ethyl phenol,  
12 isopropyl phenol, p-tertiary butyl phenol, and n-octyl phenol. Ethers  
13 are represented by the general formula ROR'. In the formula, R and R'  
14 each denote an alkyl, alkenyl, cycloalkyl, aryl, or aralkyl group of 1  
15 to 12 carbon atoms, providing that R and R' may be equal to or  
16 different from each other. Concrete examples of such ethers are  
17 diethyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether,  
18 diisoamyl ether, di-2-ethylhexyl ether, diallyl ether, ethylallyl  
19 ether, butylallyl ether, diphenyl ether, anisol, and ethylphenyl  
20 ether. Any of the compounds cited above as examples of halogen-  
21 containing alcohols is also usable.

#### 22 (E) Titanium Compound

23 Titanium compounds are divalent, trivalent, and tetravalent  
24 titanium compounds. Concrete examples of such titanium compounds are  
25 titanium tetrachloride, titanium tetrabromide, trichloroethoxy  
26 titanium, trichlorobutoxy titanium, dichlorodiethoxy titanium,  
27 dichlorodibutoxy titanium, dichlorodiphenoxy titanium, chlorotriethoxy  
28 titanium, chlorotributoxy titanium, tetrabutoxy titanium, and titanium  
29 trichloride. Among other titanium compounds enumerated above, such  
30 tetravalent titanium halides such as titanium tetrachloride,  
31 trichloroethoxy titanium, dichlorodibutoxy titanium, and dichloro-  
32 diphenoxy titanium prove desirable and titanium tetrachloride proves  
33 particularly desirable.

#### 34 Method for Preparation of Catalyst Component

35 The catalyst component of the present invention is obtained  
36 by contacting a reaction product comprising (a) a metal oxide  
37 (hereinafter referred to as "A component"), the organic Mg  
38 (hereinafter referred to as "B component"), and the halogen-containing

1 alcohol (hereinafter referred to as "C component") (b) with an  
2 electron-donating compound (hereinafter referred to as "D component")  
3 and a titanium compound (hereinafter referred to as "E component").

4 Contact of A Component, B Component, and C Component

5 The contact of A component, B component and C component is  
6 effected by (1) a procedure of first establishing contact between A  
7 component and B component and then introducing C component into  
8 contact therewith, (2) a procedure of first establishing contact  
9 between A component and C component and then introducing B component  
10 into contact thereof, (3) a procedure of first establishing contact  
11 between B component and C component and then introducing A component  
12 into contact therewith, or (4) a procedure of establishing contact  
13 among A component, B component and C component all at once.

14 The contact mentioned above, for example, is effected by  
15 stirring the relevant components in the presence or absence of an  
16 inactive medium or by mechanically comminuting the relevant component  
17 jointly.

18 Examples of the inactive medium usable in the contact are  
19 hydrocarbons such as pentane, hexane, heptane, octane, decane, cyclo-  
20 hexane, benzene, toluene, and xylene and halides of hydrocarbons such  
21 as 1,2-dichloroethane, 1,2-dichloropropane, carbon tetrachloride,  
22 butyl chloride, isoamyl chloride, bromobenzene, and chlorotoluene.

23 The contact of A component, B component and C component is  
24 generally carried out at a temperature of  $-20^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$  for a period  
25 of 0.1 to 100 hours. Where the contact entails evolution of heat,  
26 there may be adopted a procedure of first mixing the components  
27 gradually at a low temperature and, after all the components have been  
28 wholly mixed, elevating the temperature and continuing the contact.  
29 Further during the course of the contact of the components, the  
30 individual components may be washed with the aforementioned inactive  
31 medium. The proportions in which A component, B component, and C  
32 component are used in the contact are such that the mol ratio B/A  
33 falls in the range of 0.01 to 10, that of C/A in the range of 0.01 to  
34 10, and that of C/B in the range of 0.1 to 20.

35 The solid product obtained by the contact of A component, B  
36 component and C component (hereinafter referred to as "reaction  
37 product I") is subjected to the subsequent contact. Optionally, the

1 reaction product I may be cleaned with a suitable cleaning agent such  
2 as, for example, the aforementioned inactive medium.

3 Contact with D Component and E Component

4 The contact of the reaction product I with an electron-  
5 donating (D component) and a titanium compound (E component) is  
6 effected by (1) a procedure of first establishing contact between the  
7 reaction product I and D component and then introducing E component  
8 into contact therewith, (2) a procedure of first establishing contact  
9 between the reaction product I and E component and then introducing D  
10 component into contact therewith, or (3) a procedure of establishing  
11 contact between D component and E component used jointly on one part  
12 and the reaction product I on the other part.

13 The contact mentioned above is accomplished by mechanically  
14 comminuting the relevant components jointly or stirring them in the  
15 presence or absence of an inactive medium. It is more desirably  
16 effected by stirring the relevant components in the presence or  
17 absence of an inactive medium. As the inactive medium, any of the  
18 aforementioned compounds can be used effectively.

19 When the contact of the reaction product I with D component  
20 and C component is effected by their mechanical joint comminution, it  
21 is effected generally at a temperature in the range of 0°C to 200°C  
22 for a period of 0.1 to 100 hours. When the contact is carried out by  
23 stirring, it is effected generally at a temperature of 0°C to 200°C  
24 for a period of 0.5 to 20 hours. The amount of D component used in  
25 this contact is in the range of 0.05 to 10 gram mols, preferably 0.01  
26 to 1 gram mol, per gram atom of magnesium in the reaction product I.  
27 The amount of E component used in the contact is above the level of  
28 0.1 gram mol, preferably in the range of 1 to 50 gram mols, per gram  
29 atom of magnesium in the reaction product I.

30 The contact between the reaction product I and E component  
31 may be carried out twice or more. This contact can be effected by any  
32 of the procedures mentioned above. In this case, the product from the  
33 former contact may be cleaned with an inactive medium and the cleaned  
34 product allowed to contact with a freshly added portion of E component  
35 (in conjunction with the aforementioned medium).

36 Where the contact with E component is carried out in two or  
37 more split steps, the reaction mixture under treatment may be allowed

1 to contact with an inactive hydrocarbon, halide of hydrocarbon, or  
2 metal halide compound between the split steps of contact.

3 Examples of the inactive hydrocarbon usable for the contact  
4 are aliphatic, alicyclic, and aromatic hydrocarbons. Concrete  
5 examples of such hydrocarbons are n-hexane, methyl hexane, dimethyl  
6 hexane, ethyl hexane, ethylmethyl pentane, n-heptane, methyl heptane,  
7 trimethyl pentane, dimethyl heptane, ethyl heptane, trimethyl hexane,  
8 trimethyl heptane, n-octane, methyl octane, dimethyl octane,  
9 n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane,  
10 n-hexadecane, n-octadecane, n-nonadecane, n-eicosane, cyclopentane,  
11 cyclohexane, methyl cyclopentane, cycloheptane, dimethyl cyclopentane,  
12 methyl cyclohexane, ethyl cyclopentane, dimethyl cyclohexane, ethyl  
13 cyclohexane, cyclooctane, indane, n-butyl cyclohexane, isobutyl  
14 cyclohexane, adamantane, benzene, toluene, xylene, ethylbenzene,  
15 tetramethylbenzene, n-butylbenzene, isobutylbenzene, propyl toluene,  
16 decalin, and tetralin.

17 Examples of the halide of hydrocarbon usable for the contact  
18 are mono- and poly-halogen substitution products of saturated or  
19 unsaturated aliphatic, alicyclic, and aromatic hydrocarbons. Concrete  
20 examples of such compounds are aliphatic compounds such as methyl  
21 chloride, methyl bromide, methyl iodide, methylene chloride, methylene  
22 bromide, methylene iodide, chloroform, bromoform, iodoform, carbon  
23 tetrachloride, carbon tetrabromide, carbon tetraiodide, ethyl  
24 chloride, ethyl bromide, ethyl iodide, 1,2-dichloroethane, 1,2-  
25 dibromo-ethane, 1,2-diiodo-ethane, methyl chloroform, methyl bromo-  
26 form, methyl iodoform, 1,1,2-trichloro-ethylene, 1,1,2-tribromo-  
27 ethylene, 1,1,2,2-tetrachloro-ethylene, pentachloro-ethane,  
28 hexachloro-ethane, hexabromo-ethane, n-propyl chloride, 1,2-dichloro-  
29 propane, hexachloro-propylene, octachloro-propane, decabromobutane,  
30 and chlorinated paraffins, alicyclic compounds such as chlorocyclo-  
31 propane, tetrachlorocyclo-pentane, hexachloro-pentane, and hexachloro  
32 cyclohexane, and aromatic compounds such as chlorobenzene, bromo-  
33 benzene, o-dichlorobenzene, p-dichlorobenzene, hexachlorobenzene,  
34 hexabromobenzene, benzotrichloride, and p-chlorobenzo-trichloride.

35 These compounds are such that one member of a mixture of two  
36 or more members selected from the compounds enumerated above may be  
37 advantageously used.

1           The metal halide compound is the halide of one element  
2 selected from the class of elements of Group IIIa, Group IVa, and  
3 Group Va in the Periodic Table of Elements (hereinafter referred to as  
4 "metal halide"). Examples of the metal halide are chlorides,  
5 fluorides, bromides, and iodides of B, Al, Ga, In, Tl, Si, Ge, Sn, Pb,  
6 As, Sb, and Bi. Among other metal halides enumerated above,  $\text{BCl}_3$ ,  
7  $\text{BBr}_3$ ,  $\text{BI}_3$ ,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{AlI}_3$ ,  $\text{GaCl}_3$ ,  $\text{GaBr}_3$ ,  $\text{InCl}_3$ ,  
8  $\text{TlCl}_3$ ,  $\text{SiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{SbCl}_5$ , and  $\text{SbF}_5$  prove particularly  
9 desirable.

10           The contact of the reaction mixture optionally made with the  
11 inactive hydrocarbon, halide of hydrocarbon, or metal halide (herein-  
12 after referred to as "F component") between the two or more split  
13 steps of contact made by the E component is carried out at a tempera-  
14 ture in the range of  $0^\circ$  to  $200^\circ\text{C}$  for a period of 5 minutes to 20  
15 hours, preferably at  $20^\circ\text{C}$  to  $150^\circ\text{C}$  for 10 minutes to 5 hours. When  
16 the F component is a liquid substance, it is desired to be used in  
17 such an amount that the reaction product I is obtained in an amount in  
18 the range of 1 to 1,000 g per liter of the F component. When the F  
19 component is a solid substance, this solid F component is desired to  
20 be used as dissolved in another F component capable of dissolving the  
21 solid F component. The amount of this solid F component is desired to  
22 be such that the reaction product I is obtained in an amount in the  
23 range of 0.01 to 100 g per g of the F component.

24           The mass of contact between the reaction product I with the  
25 component E may be allowed to contact with the F component. This  
26 contact can be carried out in the same manner as in the contact  
27 optionally made by the use of the aforementioned F component.

28           The contact reaction product obtained as described above is  
29 cleaned, when necessary, with hydrocarbon such as hexane, heptane,  
30 octane, cyclohexane, benzene, toluene, or xylene, and then dried to  
31 give birth to the catalyst component of the present invention.

32           The catalyst component of the present invention is formed of  
33 particles having a specific surface area in the range of 10 to 1,000  
34  $\text{m}^2/\text{g}$  and a pore volume in the range of 0.5 to  $5 \text{ cm}^3/\text{g}$  as measured  
35 by the BET method at the adsorption temperature of liquefied nitrogen  
36 and possessing diameters so uniform as to be distributed in a narrow  
37 range. As to percentage composition, this catalyst component  
38 comprises 3 to 90% by weight of metal oxide, 1 to 25% by weight of

1 magnesium, 0.5 to 10% by weight of titanium, and 4 to 60% by weight of  
2 chlorine.

3 Catalyst for the Polymerization of Olefins

4 The catalyst component of the present invention is used, as  
5 combined with an organic compound of a metal selected from the class  
6 of metals belonging to Groups I through III in the Periodic Table of  
7 Elements, for catalyzing the homopolymerization of an olefin or the  
8 copolymerization of the olefin with other olefins.

9 Organic Compound of Metal of Group I through Group III

10 Examples of the organic metal compounds usable in combination  
11 with the catalyst component are organic compounds of lithium,  
12 magnesium, calcium, zinc, and aluminum. Among other organic metal  
13 compounds just mentioned, organic aluminum compounds prove  
14 particularly desirable. The organic aluminum compounds usable herein  
15 are represented by the general formula  $R_nAlX_{3-n}$  (wherein R denotes  
16 an alkyl group or an aryl group, X denotes a halogen atom, an alkoxy  
17 group or a hydrogen atom, and n denotes a desired number in the range  
18 of  $1 \leq n \leq 3$ ). Particularly desirable examples of the organic  
19 aluminum compounds are alkyl aluminum compounds such as trialkyl  
20 aluminum, dialkyl aluminum monohalide, monoalkyl aluminum dihalide,  
21 alkyl aluminum sesquihalide, dialkyl aluminum monoalkoxide, and  
22 dialkyl aluminum monohydride, respectively having 1 to 18 carbon  
23 atoms, preferably 2 to 6 carbon atoms, and mixtures and complex  
24 compounds thereof. Concrete examples of such organic aluminum  
25 compounds are trialkyl aluminums such as trimethyl aluminum, triethyl  
26 aluminum, tripropyl aluminum, triisobutyl aluminum, and trihexyl  
27 aluminum, dialkyl aluminum monohalides such as dimethyl aluminum  
28 chloride, diethyl aluminum chloride, diethyl aluminum bromide, diethyl  
29 aluminum iodide, and diisobutyl aluminum chloride, monoalkyl aluminum  
30 dihalides such as methyl aluminum dichloride, ethyl aluminum  
31 dichloride, methyl aluminum dibromide, ethyl aluminum dibromide, ethyl  
32 aluminum diiodide, and isobutyl aluminum dichloride, alkyl aluminum  
33 sesquihalides such as ethyl aluminum sesquichloride, dialkyl aluminum  
34 monoalkoxides such as dimethyl aluminum methoxide, diethyl aluminum  
35 ethoxide, diethyl aluminum phenoxide, dipropyl aluminum ethoxide,  
36 diisobutyl aluminum ethoxide, and diisobutyl aluminum phenoxide, and  
37 dialkyl aluminum hydrides such as dimethyl aluminum hydride, diethyl  
38 aluminum hydride, dipropyl aluminum hydride, and diisobutyl aluminum

1 hydride. Among other organic aluminum compounds enumerated above,  
2 trialkyl aluminums, specifically triethyl aluminum, triisobutyl  
3 aluminum, prove particularly desirable. The trialkyl aluminum can be  
4 used in combination with other organic aluminum compounds such as  
5 diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum  
6 sesquichloride, diethyl aluminum ethoxide, or diethyl aluminum hydride  
7 which is easily available commercially. These other organic aluminum  
8 compounds may be used in the form of a mixture or complex compound.

9 Further, an organic aluminum compound having two or more  
10 aluminum atoms linked through the medium of an oxygen atom or nitrogen  
11 atom is also usable. Concrete examples of this organic aluminum  
12 compound are  $(C_2H_5)_2AlOAl(C_2H_5)_2$ ,  $(C_4H_9)_2AlOAl(C_4H_9)_2$ , and  
13  $(C_2H_5)_2AlNAl(C_2H_5)_2$ .



15  
16 Examples of organic compounds of metals other than aluminum  
17 are diethyl magnesium, ethyl magnesium chloride, diethyl zinc and such  
18 compounds as  $LiAl(C_2H_5)_4$  and  $LiAl(C_7H_{15})_4$ .

19 The organic metal compound may be used independently or in  
20 combination with an electron-donating compound. This electron-  
21 donating compound may be any of the electron-donating compounds  
22 employed in the preparation of the catalyst component described  
23 above. Besides, organic silicon compounds capable of serving as  
24 electron-donating compounds and electron-donating compounds containing  
25 hetero atoms such as nitrogen, sulfur, oxygen, and phosphorus atoms are  
26 also usable.

27 Concrete examples of organic silicon compounds are  
28 tetramethoxy silane, tetraethoxy silane, tetrabutoxy silane, tetra-  
29 isobutoxy silane, tetraphenoxy silane, tetra(p-methylphenoxy) silane,  
30 tetrabenzoyloxy silane, methyl trimethoxy silane, methyl triethoxy  
31 silane, methyl tributoxy silane, methyl triphenoxy silane, ethyl  
32 triethoxy silane, ethyl triisobutoxy silane, ethyl triphenoxy silane,  
33 butyl trimethoxy silane, butyl triethoxy silane, butyl triphenoxy  
34 silane, isobutyl triisobutoxy silane, vinyl triethoxy silane, allyl  
35 trimethoxy silane, phenyl trimethoxy silane, phenyl triethoxy silane,  
36 benzyl triphenoxy silane, methyl triallyloxy silane, dimethyl  
37 dimethoxy silane, dimethyl diethoxy silane, dimethyl diisopropoxy

1 silane, dimethyl dibutoxy silane, dimethyl dihexyloxy silane, dimethyl  
2 diphenoxy silane, diethyl diethoxy silane, diethyl diisobutoxy silane,  
3 diethyl diphenoxy silane, dibutyl diisopropoxy silane, dibutyl  
4 dibutoxy silane, dibutyl diphenoxy silane, diisobutyl diethoxy silane,  
5 diisobutyl diisobutoxy silane, diphenyl dimethoxy silane, diphenyl  
6 diethoxy silane, diphenyl dibutoxy silane, dibenzyl diethoxy silane,  
7 divinyl diphenoxy silane, diallyl dipropoxy silane, diphenyl  
8 diallyloxy silane, methylphenyl dimethoxy silane, and chlorophenyl  
9 diethoxy silane.

10 Concrete examples of the electron-donating compound  
11 containing a hetero atom are such nitrogen atom-containing compounds  
12 as 2,2,6,6-tetramethyl piperidine, 2,6-dimethyl piperidine, 2,6-  
13 diethyl piperidine, 2,6-diisopropyl piperidine, 2,2,5,5-tetramethyl  
14 pyrrolidine, 2,5-dimethyl pyrrolidine, 2,5-diethyl pyrrolidine,  
15 2,5-diisopropyl pyrrolidine, 2-methyl pyridine, 3-methyl pyridine,  
16 4-methyl pyridine, 1,2,4-trimethyl piperidine, 2,5-dimethyl piper-  
17 idine, methyl nicotinate, ethyl nicotinate, nicotinic acid amide,  
18 benzoic acid amide, 2-methyl pyrrole, 2,5-dimethyl pyrrole, imidazole,  
19 toluic acid amide, benzonitrile, acetonitrile, aniline, para-  
20 toluidine, ortho-toluidine, meta-toluidine, triethyl amine, diethyl  
21 amine, dibutyl amine, tetramethylene diamine, and tributyl amine, such  
22 sulfur atom-containing compounds as thiophenol, thiophene, ethyl  
23 2-thiophene carboxylate, ethyl 3-thiophene carboxylate, 2-methyl  
24 thiophene, methyl mercaptan, ethyl mercaptan, isopropyl mercaptan,  
25 butyl mercaptan, diethyl thioether, methyl benzenesulfonate, methyl  
26 sulfite, and ethyl sulfite, such oxygen atom-containing compounds as  
27 tetrahydrofuran, 2-methyl tetrahydrofuran, 3-methyl tetrahydrofuran,  
28 dioxane, dimethyl ether, diethyl ether, dibutyl ether, diisoamyl  
29 ether, diphenyl ether, anisole, acetophenone, acetone, methylethyl  
30 ketone, acetyl acetone, ethyl 2-furalate, isoamyl 2-furalate, methyl  
31 2-furalate, and propyl 2-furalate, and such phosphorus atom-containing  
32 compounds as triphenyl phosphine, tributyl phosphine, triphenyl  
33 phosphite, tribenzyl phosphite, diethyl phosphate, and diphenyl  
34 phosphate.

35 These electron-donating compounds are such that two or more  
36 members selected from the group of compounds enumerated above can be  
37 used as a mixture. The electron-donating compound may be used at the



1 same time that the organic metal compound is used in combination with  
2 the catalyst component or it may be used after it has been placed in  
3 contact with the organic metal compound.

4 The amount of the organic metal compound to be used relative  
5 to the catalyst component of the present invention falls generally in  
6 the range of 1 to 2000 gram mols, preferably 20 to 500 gram mols, per  
7 gram atom of titanium present in the catalyst component.

8 The proportions of the organic metal compound and the  
9 electron-donating compound are such that the amount of the organic  
10 metal compound falls in the range of 0.1 to 40 gram atoms, preferably  
11 1 to 25 gram atoms, per mol of the electron-donating compound.

#### 12 Polymerization of Olefins

13 The catalyst which comprises the catalyst component obtained  
14 as described above and the organic metal compound (and the  
15 electron-donating compound) is useful for catalyzing homopolymeriza-  
16 tion of a monoolefin of 2 to 10 carbon atoms or copolymerization of  
17 the monoolefin in combination with other monoolefins or diolefins of 3  
18 to 10 carbon atoms. The catalyst exhibits an outstanding function,  
19 particularly in catalyzing homopolymerization of an alpha-olefin such  
20 as, for example, propylene, 1-butene, 4-methyl-1-pentene, or 1-hexene,  
21 copolymerization of two such alpha-olefins and/or random and block  
22 copolymerization of the alpha-olefin with ethylene.

23 The polymerization may be carried out in either the gaseous  
24 phase or the liquid phase. When the polymerization is performed in  
25 the liquid phase, it can be effected on a liquid monomer in an  
26 inactive hydrocarbon such as normal butane, iso-butane, normal pen-  
27 tane, iso-pentane, hexane, heptane, octane, cyclohexane, benzene,  
28 toluene, or xylene. The polymerization temperature falls generally in  
29 the range of -80°C to +150°C, preferably in the range of 40°C to  
30 120°C. The polymerization pressure is sufficient in the range of 1 to  
31 60 atmospheres. Adjustment of the molecular weight of the polymer to  
32 be obtained is attained by causing the polymerization to proceed in  
33 the presence of hydrogen or other known molecular weight adjusting  
34 agents. The amount of the other olefin with which the olefin is  
35 copolymerized generally is not allowed to exceed 30% by weight and  
36 preferably is selected in the range of 0.3 to 15% by weight. The  
37 polymerization by the catalyst system of this invention can be carried

1 out continuously or batchwise under those conditions which are  
2 generally adopted for the purpose of polymerization. The copoly-  
3 merization may be performed in one step or in two or more split  
4 steps.

5 Effect of the Invention

6 The catalyst component of the present invention functions  
7 effectively as a catalyst for the production of a polyolefin,  
8 particularly isotactic polypropylene, a random copolymer of ethylene  
9 and propylene, and a block copolymer of ethylene and propylene.

10 The polymerization catalyst using the catalyst component of  
11 the present invention possesses high polymerization activity and high  
12 stereoregularity and permits the high polymerization activity to be  
13 retained long during the course of the polymerization. The olefin  
14 polymer powder consequently obtained has high bulk density. The  
15 polymer powder abounds with fluidity.

16 EXAMPLE

17 The present invention will be described more specifically  
18 below with reference to working examples and applied examples. The  
19 examples are for purposes of illustrating the invention and should not  
20 be interpreted as a limitation of the invention. The percents (%)  
21 mentioned in the working examples and the applied examples are per-  
22 cents by weight unless otherwise specified.

23 The heptane insolubles content (hereinafter referred to as  
24 "HI") which shows the proportion of crystalline polymer to the whole  
25 of a given polymer represents the residue after 6 hours extraction of  
26 the polymer with boiling n-heptane in an improved version of Soxhlet  
27 extractor. The melt flow rate (MFR) represents the value determined  
28 in accordance with ASTM D-1238. The bulk density represents the value  
29 determined by the method A defined in ASTM D-1895-69.

30 EXAMPLE 1

31 Contact of Silicon Oxide with n-Butylethyl Magnesium

32 A flask having an inner volume of 200 ml and provided with a  
33 dropping funnel and a stirrer has its interior air displaced with  
34 nitrogen gas. In the flask, 5 g of silicon oxide (product of Davison  
35 Corp. having a specific surface area of  $302 \text{ m}^2/\text{g}$ , a pore volume of  
36  $1.54 \text{ cm}^3/\text{g}$ , and an average pore radius of  $204 \text{ \AA}$  and marketed under  
37 the trademark designation of G-952)(hereinafter referred to as  
38 " $\text{SiO}_2$ ") fired under a flow of nitrogen gas at  $200^\circ\text{C}$  for two hours

1 and further at 700°C for five hours and 20 ml of n-heptane were  
2 placed. The compounds so placed and 20 ml of a 20% n-heptane solution  
3 of n-butylethyl magnesium (hereinafter referred to as "BEM") (the  
4 solution in the amount of 26.8 mmol as BEM) added thereto were stirred  
5 at 90°C for two hours. The supernatant consequently formed was  
6 removed by decantation and the solid was washed with 50 ml of  
7 n-heptane at room temperature and the supernatant formed again was  
8 removed by decantation. The washing treatment with n-heptane was  
9 repeated four more times.

#### 10 Contact with 2,2,2-trichloroethanol

11 The solid product issuing from the last washing treatment was  
12 suspended in 20 ml of n-heptane. Into the resultant suspension, a  
13 solution of 9.6 g (64 mmols) of 2,2,2-trichloroethanol in 10 ml of  
14 n-heptane was added dropwise through the dropping funnel at 0°C over a  
15 period of 30 minutes. The suspension and the added solution were  
16 stirred at 0°C for one hour, heated to 80°C over a period of one hour  
17 and again stirred at 80°C for one hour. After the completion of the  
18 reaction, the reaction mixture at room temperature was washed twice  
19 with 50 ml of n-heptane and three times with 50 ml of toluene. The  
20 solid consequently obtained (solid component I), by analysis, was  
21 found to contain 49.5% of  $\text{SiO}_2$ , 3.8% of magnesium, and 33.5% of  
22 chlorine. This solid was found to have a specific surface area of 255  
23  $\text{m}^2/\text{g}$  and a pore volume of  $0.79 \text{ cm}^3/\text{g}$ .

#### 24 Contact with d-n-butyl phthalate and titanium tetrachloride

25 The solid component I obtained in the preceding procedure and  
26 20 ml of toluene and 0.6 g of di-n-butyl phthalate added thereto were  
27 heated for reaction at 50°C for two hours. Then, the reaction mixture  
28 and 30 ml of titanium tetrachloride added thereto were heated for  
29 reaction at 90°C for two hours. The solid substance obtained by this  
30 reaction was washed at room temperature eight times with 50 ml of  
31 n-hexane. It was then dried under a vacuum at room temperature for  
32 one hour. Consequently, 7.5 g of a catalyst component was obtained.  
33 This catalyst component was found to have a specific surface area of  
34  $285 \text{ m}^2/\text{g}$  and a pore volume of  $0.87 \text{ cm}^3/\text{g}$ . This catalyst component  
35 was found to contain 55.9% of  $\text{SiO}_2$ , 4.3% of magnesium, 16.3% of  
36 chlorine, and 3.1% of titanium.

#### 37 EXAMPLE 2

38 The solid substance formed after contact with titanium

1 tetrachloride in the procedure of Example 1 was separated. This solid  
2 substance and 30 ml of titanium tetrachloride added thereto were  
3 heated for reaction at 90°C for two hours. The solid substance  
4 consequently formed was treated in the same way as in Example 1, to  
5 afford a catalyst component having a titanium content of 2.8%.

6 EXAMPLE 3

7 The reaction mixture formed after contact with titanium  
8 tetrachloride in the procedure of Example 1 was decanted to expel the  
9 supernatant. The solid substance which remained was cleaned in 50 ml  
10 of toluene at 90°C for 15 minutes. The washing treatment with toluene  
11 was repeated. The washed solid substance and 20 ml of toluene, and 30  
12 ml of titanium tetrachloride added thereto were heated for reaction at  
13 90°C for two hours. The resultant reaction mixture was washed with  
14 n-hexane and dried in the same way as in Example 1, to afford 7.4 g of  
15 a catalyst component. This catalyst component was found to have a  
16 specific surface area of 279 m<sup>2</sup>/g and a pore volume of 0.90 m<sup>3</sup>/g.  
17 It was found to contain 56.5% of SiO<sub>2</sub>, 4.4 g of magnesium, 15.1% of  
18 chloride, and 2.4% of titanium.

19 EXAMPLE 4

20 The procedure of Example 3 was repeated, except that the  
21 temperature of contact with titanium tetrachloride was changed from  
22 90°C to 120°C. Consequently, there was prepared a catalyst component  
23 having a titanium content of 2.1%.

24 EXAMPLE 5

25 The procedure of Example 3 was repeated, except that in the  
26 contact of di-n-butyl phthalate and titanium tetrachloride, these two  
27 compounds were added at the same time for reaction. Consequently,  
28 there was prepared a catalyst component having a titanium content of  
29 2.5%.

30 EXAMPLE 6

31 The procedure of Example 3 was repeated, except that in the  
32 contact of di-n-butyl phthalate and titanium tetrachloride, 30 ml of  
33 titanium chloride was added and abruptly heated to 90°C while under  
34 stirring, 0.6 g of di-n-butyl phthalate was added subsequently and  
35 heated for reaction at 90°C for two hours. Consequently, there was  
36 prepared a catalyst component having a titanium content of 2.4%.

37 EXAMPLE 7

38 The solid component I obtained in the procedure of Example 1

and 50 ml of titanium tetrachloride added thereto were stirred and heated suddenly to 90°C. The resultant mixture and 0.6 g of di-n-butyl phthalate added thereto were heated for reaction at 90°C for two hours. After completion of the reaction, the supernatant was removed and the residue and 50 ml of titanium tetrachloride added thereto were heated for reaction at 90°C for two hours. The resultant reaction mixture was washed and dried by following the procedure of Example 1, to afford a catalyst component having a titanium content of 3.3%.

#### EXAMPLE 8

In the procedure of Example 7, between the two split steps of contact with titanium tetrachloride, the reaction mixture was washed twice with 50 ml of titanium tetrachloride at 90°C for 15 minutes. The reaction mixture was washed and dried by following the procedure of Example 1. Consequently, there was prepared a catalyst component having a titanium content of 3.0%.

#### EXAMPLES 9-11

The procedure of Example 3 was followed, except that in the contact of di-n-butyl phthalate and titanium tetrachloride, xylene (Example 9), n-heptane (Example 10), and 1,2-dichloroethane (Example 11) were severally used as an inactive medium in the place of toluene. Consequently, there were prepared catalyst components having titanium contents of 2.2% (Example 9), 3.5% (Example 10), and 2.8% (Example 11).

#### EXAMPLES 12-14

During the course of contact with di-n-butyl phthalate and titanium tetrachloride in the procedure of Example 3, the reaction mixture resulting from the first step of contact with titanium tetrachloride was freed of the supernatant. The residue and 50 ml of toluene and 3 g of silicon tetrachloride (Example 12), 3 g of aluminum trichloride (Example 13), or 3 g of hexachloroethane (Example 14) added thereto were heated for reaction at 60°C for one hour. The resultant reaction mixture was washed four times with 50 ml of toluene at 60°C. The washed reaction mixture was mixed with 20 ml of toluene and 30 ml of titanium tetrachloride to undergo the second reaction with titanium tetrachloride. The reaction mixture consequently obtained was washed and dried in the same way as in Example 1. Consequently, there were produced catalyst components having titanium contents of 2.1% (Example 12), 2.7% (Example 13), and 2.3% (Example

1 14) respectively.

2 EXAMPLES 15 and 16

3 A solid substance was obtained by effecting the reaction of  
4 the solid substance I with titanium tetrachloride and di-n-butyl  
5 phthalate in the same way as in Example 3. This solid substance was  
6 washed eight times with n-hexane similarly to Example 1. The washed  
7 solid substance was converted by addition of n-hexane into a slurry  
8 (4.5 g of solid substance and 6.8 g of n-hexane). The slurry was held  
9 in contact with 1.1 g of hexachloroethane and 100 ml of n-hexane  
10 (Example 15), 100 ml 1,2-dichloro-ethane (Example 16) at 50°C for 30  
11 minutes. The solid substance consequently obtained was separated by  
12 filtration at 50°C, washed with 100 ml of n-hexane at room  
13 temperature, dried under a vacuum for one hour. Consequently, there  
14 were prepared catalyst components having titanium contents of 1.6%  
15 (Example 15) and 1.4% (Example 16) respectively.

16 EXAMPLES 17-20

17 Catalyst components having titanium contents shown below in  
18 Table I were prepared by following the procedure of Example 3, except  
19 that varying metal oxides indicated below were used in the place of  
20  $\text{SiO}_2$ .

21 TABLE I

22 Example	23 Metal Oxide	24 Firing Conditions	25 Titanium Content (%)
26 17	27 $\text{Al}_2\text{O}_3$	28 200°C/2 hours	29 3.5
		30 700°C/5 hours	
31 18	32 $(\text{MgO})_2(\text{SiO}_2)_3$	33 200°C/2 hours	34 2.5
		35 500°C/5 hours	
36 19	37 Mixture of 1 kg of $\text{SiO}_2$	38 200°C/2 hours	39 2.3
	40 and 100 g of $\text{Al}_2\text{O}_3$	41 700°C/5 hours	
42 20	43 Mixture of 1 kg of $\text{SiO}_2$	44 200°C/2 hours	45 1.9
	46 and 20 g of $\text{CrO}_3$	47 700°C/5 hours	

48 EXAMPLES 21-23

49 Catalyst components having titanium contents indicated below  
50 were prepared by following the procedure of Example 3, except that  
51 varying magnesium compounds indicated below in Table II were used in  
52 the place of BEM.

TABLE II

	<u>Example</u>	<u>Organic Mg</u>	<u>Titanium Content (%)</u>
4	21	Di-n-hexyl magnesium (product of Texas Alkyls Corp., marketed under trademark designation of MAGALA <sup>®</sup> DNHM)	2.5
7	22	Di-n-butyl magnesium (0.5 mol)-triethyl aluminum (1 mol) complex (product of Texas Alkyls Corp., marketed under trademark designation of MAGALA <sup>®</sup> 0.5E)	2.4
11	23	Di-n-butyl magnesium (7.5 mols)-triethyl aluminum (1 mol) complex product of Texas Alkyls Corp., marketed under trademark designation MAGALA <sup>®</sup> 7.5E)	2.5

EXAMPLES 24-42

Catalyst components having titanium contents indicated below in Table III were prepared by following the procedure of Example 3, except that varying halogen-containing alcohols indicated below in Table III were used in the place of 2,2,2-trichloroethanol.

TABLE III

2	Example	Halogen-Containing Alcohol	Titanium Content (%)
4	24	1,1,1-Trichloro-2-propanol	2.3
5	25	B,B,B-Trichloro-tert-butanol	2.6
6	26	2,2-Dichloroethanol	2.8
7	27	1,3-Dichloro-2-propanol	2.7
8	28	2-Chloroethanol	2.3
9	29	4-Chloro-1-butanol	2.2
10	30	6-Chloro-1-hexanol	2.6
11	31	p-Chlorophenol	2.9
12	32	4-Chloro-o-cresol	2.7
13	33	2,4,6-Trichlorophenol	2.4
14	34	Tetrachlorohydroquinone	2.2
15	35	1-Bromo-2-butanol	2.6
16	36	1,3-Dibromo-2-propanol	2.5
17	37	p-Bromophenol	2.3
18	38	2,4,6-Tribromophenol	2.3
19	39	p-Iodophenol	2.7
20	40	2,4,6-Triiodophenol	2.5
21	41	2,2,2-Trifluoroethanol	2.9
22	42	p-Fluorophenol	2.2

EXAMPLES 43-67

Catalyst components having titanium contents shown below in Table IV were obtained by following the procedure of Example 3, except that varying electron-donating compounds indicated below in Table IV were used in the place of di-n-butyl phthalate during the contact with the solid component I.



TABLE IV

1			
2			Titanium
3	<u>Example</u>	<u>Electron-Donating Compound</u>	<u>Content (%)</u>
4	43	Ethyl benzoate	2.3
5	44	Diisobutyl phthalate	2.1
6	45	Phthalic anhydride	2.4
7	46	Phthalic acid dichloride	2.7
8	47	Phthalic acid n-butyl chloride	2.5
9	48	Mono-n-butyl phthalate	2.4
10	49	Benzoic anhydride	2.2
11	50	Benzoyl chloride	2.6
12	51	Ethyl cinnamate	2.4
13	52	Ethyl cyclohexane carboxylate	2.5
14	53	Tartaric acid	2.8
15	54	Di-n-butyl tartrate	2.4
16	55	Isobutyl methacrylate	2.3
17	56	Phthalic acid	2.1
18	57	Benzoic acid	3.0
19	58	Di-n-butyl maleate	3.2
20	59	Diisobutyl sebacate	2.8
21	60	Tri-n-butyl trimellitate	2.2
22	61	Ethanol	2.3
23	62	Isobutanol	2.0
24	63	2-Ethylhexanol	2.3
25	64	p-Cresol	2.1
26	65	Diethyl ether	2.0
27	66	Di-n-butyl ether	2.2
28	67	Diphenyl ether	2.5

1 EXAMPLE 682 Contact of Silicon Oxide and 2,2,2-Trichloroethanol

3 A flask having an inner volume of 200 ml and provided with a  
4 dropping funnel and a stirrer had its interior air displaced with  
5 nitrogen gas. In this flask, 5 g of the same  $\text{SiO}_2$  as used in  
6 Example 1, 40 ml of n-heptane, and 12 g of 2,2,2-trichloroethanol  
7 added thereto were stirred for contact at 90°C for two hours. After  
8 completion of the reaction, the reaction mixture was washed three  
9 times with 50 ml of n-heptane and decanted at room temperature.

10 Contact with n-butylethyl magnesium

11 The solid substance obtained in the foregoing procedure was  
12 suspended in 20 ml of n-heptane. To the resultant suspension, 11 ml  
13 of the same BEM solution as used in Example 1 was added dropwise  
14 through the dropping funnel at 0°C over a period of 30 minutes. The  
15 resultant mixture was stirred at 0°C for one hour, heated to 80°C over  
16 a period of one hour, and stirred at 80°C for one hour. After comple-  
17 tion of the reaction, the reaction mixture was washed twice with 50 ml  
18 of n-heptane and three times with 50 ml of toluene.

19 Contact with di-n-butyl phthalate and titanium tetrachloride

20 By following the procedure of Example 3, except that the  
21 solid component obtained in the preceding procedure was used instead  
22 in the contact with the di-n-butyl phthalate and titanium  
23 tetrachloride, there was obtained 7.8 g of a catalyst component having  
24 a titanium content of 2.5%.

25 EXAMPLE 6926 Contact of Silicon Oxide and 2,2,2-Trichloroethanol

27 In a mill pot, 10 g of the same  $\text{SiO}_2$  as used in Example 1  
28 and 4.4 g of 2,2,2-trichloroethanol were subjected to a crushing  
29 treatment for 24 hours.

30 Contact with n-Butylethyl Magnesium

31 A flask having an inner volume of 200 ml and provided with a  
32 dropping funnel and a stirrer had its interior air displaced with  
33 nitrogen gas. In the flask, 6 g of the solid substance obtained in  
34 the preceding procedure and comminuted and 40 ml of n-heptane were  
35 placed. Then, 9 ml of the same BEM solution as used in Example 1 was  
36 added thereto dropwise through the dropping funnel at 0°C over a  
37 period of 30 minutes. The resultant reaction mixture was thereafter  
38 treated in the same way as in Example 68 to obtain a solid component.

1 Contact with di-n-Butyl Phthalate and Titanium Tetrachloride

2 By following the procedure of Example 3, except that the  
3 solid component obtained in the preceding procedure was used instead  
4 in the contact with di-n-butyl phthalate and titanium tetrachloride,  
5 there was obtained 8.1 g of a catalyst component having a titanium  
6 content of 2.3%.

7 EXAMPLE 70

8 Contact of 2,2,2-trichloroethanol and n-butylethyl magnesium

9 A flask having an inner volume of 200 ml and provided with a  
10 dropping funnel and a stirrer had the interior air displaced with  
11 nitrogen gas. In the flask, 5 g of 2,2,2-trichloroethanol and 40 ml  
12 of n-heptanol were kept at 0°C. Then, 12.5 ml of the same BEM  
13 solution as used in Example 1 was added dropwise at 0°C over a period  
14 of 30 minutes. The contents of the flask were stirred at 0°C for one  
15 hour, then heated to 80°C over a period of one hour, and then stirred  
16 at 80°C for one hour. After completion of the reaction, the reaction  
17 mixture was washed three times with 50 ml of n-heptane at room  
18 temperature and then dried under a vacuum at room temperature for one  
19 hour. Consequently, there was obtained a solid reaction product.

20 Contact with silicon oxide

21 In a mill pot, 5 g of the solid reaction product obtained in  
22 the preceding procedure and 8 g of the same  $\text{SiO}_2$  as used in Example  
23 1 were subjected to a comminution treatment for 24 hours.

24 Contact with di-n-butyl phthalate and titanium tetrachloride

25 By following the procedure of Example 3, except that 6 g of  
26 the comminuted solid substance obtained in the preceding procedure was  
27 used instead in the contact with di-n-butyl phthalate and titanium  
28 tetrachloride, there was obtained 6.8 g of a catalyst component having  
29 a titanium content of 2.5%.

30 EXAMPLE 71

31 Contact of Silicon Oxide, n-Butylethyl Magnesium, and  
32 2,2,2-Trichloroethanol

33 A flask having an inner volume of 200 ml and provided with a  
34 dropping funnel and a stirrer had its interior air displaced with  
35 nitrogen gas. In the flask, 5 g of the same  $\text{SiO}_2$  as used in Example  
36 1 and 20 ml of n-heptane were placed. Then 30 ml of the same BEM  
37 solution as used in Example 1 was added and subsequently 12 g of  
38 2,2,2-trichloroethanol was added dropwise thereto at 0°C over a period

1 of 30 minutes. The resultant mixture was stirred at 0°C for one hour,  
2 heated to 80°C over a period of one hour, and stirred at 80°C for one  
3 hour. After completion of the reaction, the reaction mixture was  
4 washed twice with 50 ml of n-heptane and three times with 50 ml of  
5 toluene at room temperature, to obtain a solid component.

6 Contact with di-n-butyl phthalate and titanium tetrachloride

7 By following the procedure of Example 3, except that the  
8 solid component obtained in the preceding procedure was used instead  
9 in the contact of di-n-butyl phthalate and titanium tetrachloride,  
10 there was obtained 7.5 g of catalyst component having a titanium  
11 content of 2.6%.

12 APPLIED EXAMPLE 1

13 In a stainless steel autoclave having an inner volume of 1.5  
14 liters and provided with a stirrer, a reaction mixture obtained by  
15 mixing 30.3 mg of the catalyst component prepared by the procedure of  
16 Example 1, 0.97 ml of a solution containing 1 mol of triethyl aluminum  
17 (hereinafter referred to as "TEAL") per liter of n-heptane, and 0.97  
18 ml of a solution containing 0.1 mol of phenyl triethoxy silane  
19 (hereinafter referred to as "PES") per liter of n-heptane and allowing  
20 the resultant mixture to stand for five minutes was placed under a  
21 blanket of nitrogen gas. Then, 0.1 liter of hydrogen gas as a  
22 molecular weight regulator and 1 liter of liquefied propylene were  
23 introduced therein under pressure. The reaction system was heated to  
24 70°C to effect polymerization of propylene for one hour. After  
25 completion of the polymerization, the unaltered propylene was purged  
26 to produce 105 g of white polypropylene powder having 97.6% of HI, 4.7  
27 of MFR, and 0.42 g/cm<sup>3</sup> of bulk density [Kc (amount of produced  
28 polymer in g per g of catalyst component) = 3,500 and Kt (amount of  
29 produced polymer in kg per g of titanium in catalyst component) = 113].

30 APPLIED EXAMPLES 2-71

31 Polymerization of propylene was carried out by following the  
32 procedure of Applied Example 1, except that the catalyst components  
33 obtained in Examples 2-71 were severally used. The results are shown  
34 in Table VI. The polypropylene powder obtained in Applied Example 3  
35 was tested for particle diameter distribution. The results are shown  
36 in Table V below.

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TABLE V

<u>Particle diameter (μm)</u>		<u>Proportion of distribution (%)</u>
Less than 149		0
149 - 250		0.1
250 - 350		2.3
350 - 420		5.9
420 - 590		24.9
590 - 840		42.3
840 - 1,000		12.8
1,000 - 1,680		11.6
Exceeding 1,680		0.1

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TABLE VI

<u>Applied Catalyst</u>		<u>Kc</u>	<u>Kt</u>	<u>HI</u>	<u>MFR</u>	<u>Bulk Density</u>
<u>Example</u>	<u>Component</u>	<u>(g/g Cat)</u>	<u>(kg/g Ti)</u>	<u>(%)</u>	<u>(g/10 min)</u>	<u>(g/cm<sup>3</sup>)</u>
2	Example 2	3,200	114	97.5	4.5	0.42
3	" 3	4,300	179	98.1	4.7	0.44
4	" 4	3,900	186	98.0	5.1	0.43
5	" 5	3,900	156	97.9	4.0	0.43
6	" 6	4,300	179	98.4	3.9	0.45
7	" 7	3,100	94	97.7	5.5	0.43
8	" 8	3,600	120	98.0	5.0	0.44
9	" 9	4,000	182	98.0	4.2	0.43
10	" 10	3,600	103	97.9	6.2	0.40
11	" 11	3,700	132	97.5	5.8	0.42
12	" 12	3,600	171	97.8	4.9	0.41
13	" 13	3,900	144	98.2	6.0	0.43
14	" 14	3,700	161	98.0	4.9	0.42
15	" 15	3,200	200	98.2	5.4	0.44
16	" 16	3,400	243	98.3	5.9	0.45
17	" 17	3,100	89	97.8	4.5	0.43
18	" 18	2,800	112	97.3	4.8	0.41
19	" 19	2,600	113	97.2	5.3	0.40
20	" 20	2,900	153	97.6	5.8	0.41
21	" 21	3,900	156	97.8	4.3	0.44
22	" 22	3,600	150	97.6	6.2	0.42
23	" 23	3,500	140	97.5	5.8	0.43
24	" 24	3,900	170	97.9	4.3	0.44

TABLE VI, (cont.)

							Bulk
	Applied	Catalyst		Kc	Kt	HI	Density
	Example	Component		(g/g Cat)	(kg/g Ti)	(%)	(g/cm <sup>3</sup> )
5	25	Example 25		4,100	158	98.0	0.43
6	26	" 26		3,600	129	97.7	0.43
7	27	" 27		2,900	107	97.5	0.43
8	28	" 28		3,200	139	97.6	0.43
9	29	" 29		3,200	145	97.4	0.42
10	30	" 30		2,900	112	97.3	0.43
11	31	" 31		3,600	124	97.7	0.43
12	32	" 32		3,300	122	97.8	0.41
13	33	" 33		3,700	154	97.6	0.42
14	34	" 34		2,700	123	97.6	0.43
15	35	" 35		2,500	96	97.4	0.42
16	36	" 36		2,800	112	97.2	0.41
17	37	" 37		3,100	135	97.1	0.43
18	38	" 38		2,900	126	97.3	0.43
19	39	" 39		2,600	96	97.0	0.42
20	40	" 40		2,500	100	97.4	0.41
21	41	" 41		3,100	107	97.3	0.43
22	42	" 42		2,600	118	97.3	0.42
23	43	" 43		3,000	130	97.9	0.43
24	44	" 44		3,800	181	98.2	0.43
25	45	" 45		3,200	133	98.0	0.40
26	46	" 46		3,500	130	98.1	0.40
27	47	" 47		3,100	124	98.0	0.42
28	48	" 48		3,300	138	97.9	0.41
29	49	" 49		2,900	132	97.9	0.40
30	50	" 50		2,900	112	97.8	0.40
31	51	" 51		2,700	113	97.6	0.38
32	52	" 52		2,900	116	97.8	0.39
33	53	" 53		2,800	100	97.5	0.40
34	54	" 54		2,900	121	97.6	0.40
35	55	" 55		3,100	135	97.6	0.41
36	56	" 56		3,000	143	97.8	0.40
37	57	" 57		3,000	100	97.5	0.40
38	58	" 58		2,900	91	97.6	0.41

TABLE VI, (cont.)

2							Bulk	
3	Applied	Catalyst		Kc	Kt	HI	MFR	Density
4	Example	Component		(g/g Cat)	(kg/g Ti)	(%)	(g/10 min)	(g/cm <sup>3</sup> )
5	59	Example 59		3,000	107	97.9	5.2	0.40
6	60	" 60		3,200	145	98.1	4.1	0.43
7	61	" 61		3,000	130	98.0	5.2	0.41
8	62	" 62		2,900	145	97.9	4.8	0.39
9	63	" 63		3,000	130	98.0	4.8	0.41
10	64	" 64		3,100	148	98.0	5.2	0.40
11	65	" 65		2,800	140	97.4	6.8	0.38
12	66	" 66		2,900	132	97.6	6.5	0.39
13	67	" 67		2,900	116	97.6	6.0	0.39
14	68	" 68		4,000	160	98.1	4.1	0.42
15	69	" 69		3,900	170	98.0	3.8	0.38
16	70	" 70		3,900	156	98.2	4.5	0.38
17	71	" 71		3,800	146	97.9	4.4	0.40

APPLIED EXAMPLE 72Gaseous-phase Polymerization of Propylene

In an autoclave having an inner volume of 5 liters and provided with a stirrer, 150 g of polypropylene powder dried in advance under a flow of nitrogen gas at 90°C for four hours was placed. To this autoclave, with the stirrer thereof operated at 150 rpm, the same catalyst component as prepared in Example 3 was fed at a rate of 50 mg/hr, TEAL at a rate of 0.7 mmol/hr, PES at a rate of 0.05 mmol/hr, propylene at a rate of 130 g/hr, and hydrogen gas at a rate of 15 ml/hr for continuous polymerization of propylene under the conditions of 70°C of temperature and 20 kg/cm<sup>2</sup> of pressure, with the product of polymerization continuously withdrawn from the autoclave. Consequently, there was obtained polypropylene powder at a rate of 90 g/hr. The polymer so produced was found to have an MFR of 5.2 g/10 min and an HI of 96.8%.

APPLIED EXAMPLE 73Block Copolymerization of Propylene

In an autoclave having an inner volume of 1.5 liters and provided with a stirrer, a reaction mixture obtained by mixing 30.0 mg of the catalyst component prepared by the procedure of Example 3, 0.75 ml of n-heptane solution of TEAL (1 mol/liter), and 0.75 ml of

1 n-heptane solution of PES (0.1 mol/liter) and allowing the resultant  
2 mixture to stand for five minutes was placed under a blanket of  
3 nitrogen gas. Then, 100 ml of hydrogen gas and 1 liter of liquefied  
4 propylene were introduced therein under pressure. The reaction system  
5 consequently formed was heated to 70°C to effect homopolymerization of  
6 propylene for one hour. In an experiment of polymerization performed  
7 parallelly under the same conditions, the polypropylene obtained was  
8 found to have a HI of 98.1%. After completion of the polymerization,  
9 the unaltered propylene was purged and the interior of the autoclave  
10 was displaced with nitrogen gas. Then, a mixed gas of ethylene and  
11 propylene [ethylene/propylene = 1.5 (by mol ratio)] was introduced at  
12 such a rate as to keep the monomer gas pressure at 1.5 atmospheres.  
13 Under these conditions, copolymerization was effected at 70°C for  
14 three hours. After completion of the polymerization, the unaltered  
15 mixed gas was discharged. Consequently, there was obtained 175 g of  
16 block copolymer of propylene.

17 The proportion of the copolymer fraction calculated based on  
18 the consumed amount of the mixed gas and the total amount of polymer  
19 was found to be 26.3% and the ethylene content in the total polymer  
20 was found by infrared spectral analysis to be 12.6%. Thus, the  
21 ethylene content in the copolymer fraction is found by calculation to  
22 have been 48%. The amount of the homopolymer of propylene per g of  
23 the catalyst component found based on the amount of the total polymer  
24 and the consumed amount of the mixed gas was found to be 4,300 g and  
25 the amount of the copolymer fraction formed to be 1,530 g. The block  
26 copolymer so produced was found to have a MFR of 2.9 g/10 min and a  
27 bulk density of 0.44 g/cm<sup>3</sup>. The polymer particles were free from  
28 cohesion and showed absolutely no sign of fouling in the autoclave.

#### 29 APPLIED EXAMPLE 74

##### 30 Random Copolymerization of Propylene and Ethylene

31 During the polymerization of propylene in the procedure of  
32 Applied Example 1, 0.6 g of ethylene was introduced under pressure  
33 into the autoclave six times at intervals of 10 minutes to effect  
34 random copolymerization of propylene and ethylene. After completion  
35 of the polymerization, the unaltered monomers were discharged from the  
36 polymerization system. Consequently, there was obtained 136 g of a  
37 random copolymer of propylene and ethylene. The ethylene content in  
38 the produced copolymer was found by infrared spectral analysis to be



1 2.7%. The amount of the copolymer formed per 1 g of the catalyst  
2 component was 4,500 g. The produced copolymer was found to have a MFR  
3 of 12.4 g/10 min and a bulk density of 0.43 g/cm<sup>3</sup>.

4 APPLIED EXAMPLE 75

5 Polymerization of 1-Butene

6 By following the procedure of Applied Example 1, except using  
7 205 mg of the catalyst component obtained in Example 3, 400 ml of  
8 isobutane as a medium, and 400 ml of 1-butene (liquid) in the place of  
9 liquefied propylene and carrying out the polymerization under the  
10 conditions of 40°C of temperature and five hours of duration, 1-butene  
11 was polymerized. Consequently, there was obtained 307.3 g of powdery  
12 poly-1-butene. The value, Kc, was found to be 1,500 g/g of catalyst  
13 component. The produced polymer was found to have a MFR of 4.1 g/10  
14 min, a bulk density of 0.41 g/cm<sup>3</sup>, and an ether insolubles content  
15 (residue after five hours' extraction from boiling diethyl ether) of  
16 99.3%.

17 APPLIED EXAMPLE 76

18 Polymerization of 4-methyl-1-pentene

19 By following the procedure of Applied Example 75, except  
20 using 230 mg of the catalyst component obtained by Example 3 and 400  
21 ml of 4-methyl-1-pentene in the place of 1-butene, 4-methyl-1-pentene  
22 was polymerized. Consequently, there was obtained 312.5 g of powdery  
23 poly-4-methyl-1-pentene. The value, Kc, was found to be 1,360 g/g of  
24 catalyst component. The produced polymer was found to have a MFR of  
25 3.5 g/10 min, a bulk density of 0.38 g/cm<sup>3</sup>, and an ether insolubles  
26 content of 98.5%.

## CLAIMS:

1. A titanium containing supported catalyst component comprising the product obtained by contacting

(1) a reaction product comprising

(a) an oxide, or a composite oxide, of an element of Group II, or IV of the Periodic Table,

(b) one or more dihydrocarbyl magnesium compounds or a mixture or a complex thereof with an organic compound of aluminium, boron, beryllium, or zinc, and

(c) a halogen-containing alcohol held with

(2) (d) an electron-donating compound and

(e) a di-, tri, or tetravalent titanium compound.

2. The titanium containing supported catalyst component of claim 1, wherein the metal oxide is  $\text{SiO}_2$ /

3. The titanium containing supported catalyst component of claim 1, or claim 2, wherein the dihydrocarbyl magnesium compound is represented by the general formula  $\text{RMgR}^1$  wherein R and  $\text{R}^1$ , which can be the same or different, can be an alkyl, cycloalkyl, aryl, or aralkyl group having from 1 to 20 carbon atoms.

4. The titanium containing supported catalyst component of any of claims 1 to 3 wherein the titanium compound is selected from titanium tetrachloride, trichloroethoxy titanium, dichlorodibutoxy titanium and dichlorodiphenoxy titanium.

5. The titanium containing supported catalyst component of any of claims 1 to 4 wherein the electron-donating compound carboxylic esters, carboxylic halides, alcohols, ethers, ketones, amines, amides, nitriles, aldehydes, alcoholates, phosphorous bismuth or antimony compounds bonded to an organic group through carbon or oxygen atoms, phosphamides, theoethers, thioesters, and carbonic sters.

6. The titanium containing supported catalyst component of any of claims 1 to 5 wherein the halogen-containing alcohol is a monohydric or polyhydric alcohol and the halogen atom is chlorine.

7. The titanium containing supported catalyst component of claim 6 wherein the halogen-containing alcohol is a 2,2,2-trichloroethanol.

8. A titanium containing supported catalyst component comprising the product obtained by contacting

(1) a reaction comprising

- (a)  $\text{SiO}_2$
- (b) n-butylethyl magnesium, and
- (c) 2,2,2-trichloroethanol, with
- (2) (d) di-n-butylphthalate, and
- (e) titanium tetrachloride.

9. The titanium containing supported catalyst component of any of claims 1 to 8 wherein the reaction product is contacted with the titanium compound at least two times.

10. The titanium containing supported catalyst component of claim 9 wherein the reaction product is contacted with an inactive hydrocarbon, a halide of a hydrocarbon or a metal halide between the titanium compound treatments.

11. A catalyst system for the polymerization of olefins comprising

(A) the titanium containing supported catalyst component of any of claims 1 to 8

and

(B) an organo metallic compound of an element of Groups I to Group III

12. A process for the homopolymerization of an olefin or the copolymerization of an olefin with another olefin, said process comprising polymerizing the olefin(s) in the presence of the catalyst system of claim 11.